

COLOUR AND CHEMICAL CONSTITUTION.

PART X.—A GENERAL NUMERICAL SOLUTION OF THE COLOUR-
CONSTITUTION PROBLEM.

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In Part IX of this work it was shown that the spectra and colours of a particular class of triphenylcarbinol colours (*viz.* halogenated phthaleins) could be calculated from the data of a parent-substance by multiplying by a factor dependent on the nature, number and position of the substituents.

I have now discovered that this principle can be applied to all the ordinary triphenylcarbinol dyes ("aniline dyes"), the colours of which can now be calculated, as will be seen below.

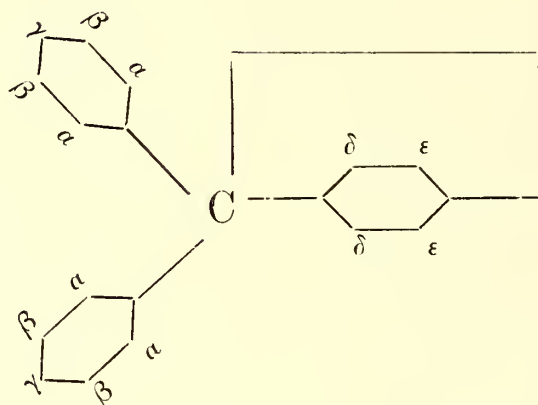
It has been shown in earlier parts of this work that the colour-phenomenon is additive, *i. e.* that each group present acts in colour-change almost independently of other groups and of the rest of the molecule.

I now find that each combination of group and position, *e. g.*, orthomethyl, parahydroxyl, etc., can be assigned a colour-factor by means of which the effect on colour of the substitution of the group for hydrogen in the given position can be calculated: even if five or six groups are present it is found that by multiplying the wave-length of the parent substance by all the factors of the groups present in a coloured substance a result is obtained which tallies closely with observation.

The apparent inconsistency between the new factorial notion and the "additive" notion is merely accidental. It is a well-known fact in mathematics that $(1 + a)(1 - b) = 1 + a - b$ without serious error unless a or b is more than $\frac{1}{10}$ or so. The "factors" are of the form $1 + a$ or $1 - b$ and the "additive" notion corresponds to the right side of the equation.

The parent-substance taken is an imaginary one,* being the anhydride of triphenylcarbinol or *p*-phenylenediphenylmethane:

* Said, however, to have been made; see Beilstein, ii, p. 292.



It would have been convenient to call this "chromane," but unfortunately Kostanecki has used this name already to denote the anhydride of *o*-oxy-phenylpropylalcohol. I shall therefore name it provisionally "fuchsene," which will indicate that it is the hydrocarbon of fuchsone.

Its fundamental wave-length is found by multiplying that of benzaurine (its di-oxy-derivative) by the square of the ratio of the wave-lengths of benzaurine and aurine (tri-oxy-derivative), *i. e.* $x = 553^3 \div 534^2 = 593$.

The ratio $\frac{\text{aurine}}{\text{benzaurine}}$ is the first of my colour-factors, and is the para (or γ) hydroxyl-factor, its value being 0.9657; and it is to be noted that it is assumed to be the same whether —OH replaces —H or :O is attached to fuchsene giving fuchsone. The theoretical wave-length of fuchsone (oxofuchsene or keto-fuchsene) if it were soluble in alkali would thus be $\lambda 593 \times 0.9657$ or $\lambda 572\frac{1}{2}$; that of oxyfuchsone or benzaurine* (oxyoxofuchsene) is $\lambda 593 \times (0.9657)^2$ or $\lambda 553$; that of aurine (dioxyfuchsone or dioxyoxofuchsene) is $\lambda 593 \times (0.9657)^3$ or $\lambda 534$.

The next ratio is the para (or γ) amino-factor, the value of which is 0.972. The calculated wave-length for "fuchsonimine" † (iminofuchsene) is $\lambda 593 \times 0.972$ or $\lambda 576$, but $\lambda 430$ was observed in alcohol, with two other bands (ratio 16 : 13 : 10), which is certainly abnormal, but if the series is really 22 : 19 : 16 : 13 : 10 the observed band, which would be about $\lambda 425$ in water, agrees well with $\frac{16}{22} \times 576$.

The calculated wave-length for the diamino-derivative, which is the well-known Doebner's violet, is $\lambda 593 \times (0.972)^2$ or $560\frac{1}{2}$. The reading $\lambda 565$ in alcohol is on record, and it is to be noted that there is no ionisation in alcohol, so that the chlorine of the coloured salt counts as part of the

* There appear to be two kinds of benzaurine. The one in the text, of $\lambda 553$, is made from *p*-oxybenzophenone and phenol, the other of $\lambda 570$ (Part I, 1917, p. 6) from benzaldehyd and phenol with oxidation. These two reactions should give the same product, but the products are undoubtedly different.

† This confusing name should be changed to fuchsimine.

molecule. From the analogy of the behaviour of fuchsine I should estimate that the ion of Doebner's violet in water would have λ about 560. My own preparation has λ 562. The calculated wave-length for the triamino-derivative of fuchsene, which is the ordinary dye parafuchsine, is λ $593 \times (0.972)^3$ or λ 544. This agrees with direct observation in water.

These two ratios can next be combined. The theoretical wave-length for oxyfuchsonimine or aminofuchsone is λ $593 \times 0.9657 \times 0.972$ or λ $556\frac{1}{2}$. Observed λ 558. That for diaminofuchsone is λ $593 \times 0.9657 \times (0.972)^2$ or λ 541. Observed λ 541. That for dioxyfuchsonimine is λ $593 \times (0.9657)^2 \times 0.972$ or λ $537\frac{1}{2}$. I have made this new substance, which is alternatively named paramino-benzaurine, and observed its wave-length to be λ 538.

The third ratio is the N-methyl-factor, which has the value 1.0245. From this the colours of all the violet and green dyes of the series can be calculated. It will be found more convenient, however, to combine the second and third factors, giving (fourthly) a γ -N-methylamino-factor, the value of which is practically unity (viz. 0.9965), and (fifthly) a γ -N-dimethylamino-factor, the value of which is 1.021.

Applying these, the theoretical colour of "fuchsonedimethylimine" (dimethylaminofuchsene) is λ 593×1.021 or λ $605\frac{1}{2}$. The only band, in water, of this substance is very broad, at about λ 460, and may be a harmonic, since $\frac{3}{4}$ of $605\frac{1}{2}$ is 454. The fraction $\frac{1.9}{2.5}$ agrees exactly: see previous page.

That of bis-dimethylaminofuchsene ("malachite green") is λ $593 \times (1.021)^2$ or λ 619, agreeing with observation. That of *tris-dimethylaminofuchsene ("crystal-violet") is calculated to be λ $593 \times (1.021)^3$ or λ 632. This agrees with observation in the green phase of crystal violet obtained by adding a trace of mineral acid to its solution (observed λ 632, but in neutral solution λ 595).† Hofmann's violet (pentamethylpararosaniline) is calculated to have wave-length λ $593 \times (1.021)^2 \times 0.9965$ or λ 616; this also agrees with the acid phase of this dye. It is to be noted that the commercial article is partly derived from orthotoluidine (methylated fuchsine or rosaniline, not parafuchsine) and therefore gives colours a shade higher up the scale.

I have also made the remaining new member of this series, dimethylaminofuchsone (dimethylamino-oxofuchsene), by condensing paraoxybenzophenone with dimethylaniline and AlCl_3 . This has a wave-length of λ 586 when neutral (violet, sparingly soluble), but develops a pink colour and two other bands, λ 500 and 530, when acid (isomers?). The calculated colour is λ $593 \times 1.021 \times 0.9657$ or λ 585. Another member of the series is "paraoxy-malachite-green," which is bis-dimethylaminofuchsone. Its calculated colour is that of the foregoing multiplied by 1.021 or λ 597, which agrees with its

* The correct Latin for thrice is *ter* but might be unintelligible.

† The violet phase is discussed later on.

described colour. My preliminary observations indicate that the band varies between λ 580 and λ 607 according to the reaction of the solution.

Perhaps it is surprising that even "iodine-green" (heptamethylparosaniline, with three methyls on one nitrogen) agrees with theory, as far as can be seen. The value of λ should be $593 \times (0.972)^3 \times (1.0245)^7$ or 645. The band observed in a commercial specimen was λ 640.

Another important point is that the effect of N-ethyl is scarcely distinguishable from that of N-methyl—the value of (6) the γ -N-diethyl-amino-factor being about 1.023 as against 1.021 for dimethylamino.

A factor for the replacement of $-\text{OH}$ by $-\text{NEt}_2$ can be calculated from the foregoing data. The process of replacing γ -OH by γ -H has the factor $1 \div 0.9657$, and the factor for replacing γ -H by γ -NEt₂ is 1.023; hence the required factor is $1.023 \div 0.9657$ or 1.061. Applying this to the case of fluorescein and rhodamine, we here use the factor with a different constant, viz. that of fluorescein, λ 494. The replacement of two hydroxyl by two diethylamino-groups should give a substance with wave-length $494 \times (1.061)^2$ or 555. Observation on commercial rhodamine gave λ 556.

Correlation of the Phthaleins with the Aniline Dyes.—We now introduce a seventh factor, namely that of the orthocarboxyl group present in the phthaleins. This factor is very close to unity, being equal to 1.002. As examples benaurine of λ 553 may be compared with phenolphthalein λ 554, and $\beta\beta'\epsilon\epsilon'$ -tetrabromobenaurine of λ 583 with tetrabromophenolphthalein of λ 584½. It will be sufficient at this stage to calculate only one or two of the observed colours. Phenoldimethylanilinephthalein (see Part II, p. 112) is the oxy-dimethylamino-carboxylic acid of fuchsene, and its calculated wave-length is $593 \times 0.9657 \times 1.021 \times 1.002$ or 587, and that was also the reading observed in the alkaline solution of this substance.

Curiously enough, bis-dimethylanilinephthalein appears to be colourless. Its wave-length should be 622, as it is the carboxylic acid of malachite-green. The sulphophthalein, however, is not colourless, but has λ 634 or λ 593 according as it is acid or neutral.

At this stage the other factors for substitution in phenolphthalein may be combined with the parahydroxy-factor so as to express the compounds investigated in Parts I to VI (see the summary on the last page of Part IV) as direct derivatives of fuchsene. The ratio of phenolphthalein to fuchsene is 0.934. Now since the value of (8) the ortho- (or ϵ -) bromine atom-factor is 1.0133 in phenolphthalein, the lengthy calculation of ϵ -tetrabromophenolphthalein from first principles as $593 \times (0.9657)^2 \times 1.002 \times (1.0133)^4$ may be shortened to $593 \times 0.934 \times (1.0133)^4$, both coming to λ 584, and agreeing with observation.

We may again repeat here the remarkable circumstance that methyl, ethyl, isopropyl, chlorine, bromine, and iodine in the ϵ -positions have all

nearly the same effect on colour, their colour-factors being 1.013 ± 0.001 (9th to 13th of the known factors); also that in the δ position the effect is twice as great, the colour-factor being $1.025 \pm .002$.

Before finishing with the phthaleins it may be noted that the behaviour of the para-position in the phthalic ring both of phenolphthalein and of fluorescein is usually abnormal—a point which is discussed in a separate communication. Another exception is oxydiphenylphthalide, which being fuchsoncarboxylic acid should have λ 574, whereas observation gave λ 560. It is very difficult to obtain this substance free from phenolphthalein, and it is excessively easily bleached by alkali, so much so that the American writers on colour describe it as colourless in alkali.

The 14th colour-factor, that of γ -methoxyl, depends on two observations only, and is therefore somewhat in doubt: its value is 0.973. This makes the γ -CH₃ in phenolphthalein-monomethylether have a factor value of 1.007, whereas the ϵ -CH₃* has, as mentioned just above, the value 1.012. The α -CH₃ and the δ -CH₃ both appear to have a value about 1.024, which is practically the same as the N-CH₃ given at the beginning (1.0245), so need not be counted as a new factor.

The 15th and 16th colour-factors are those of ϵ -hydroxyl and ϵ -methoxyl: their values are comparatively large, viz. 1.030 and 1.037 respectively. It is very significant that ϵ -OH and γ -OH are practically the reverse of one another ($1.030 \times 0.9657 = 0.9946$). An example of this is the substance catechaurine (β_3 -trioxaurine), made by condensing catechol with oxalic acid. The systematic name is β_3 - γ_3 -hexaoxyfuchsene, and its theoretical absorption is therefore $593 \times (0.9946)^3$ or $583\frac{1}{2}$, which agrees with observation (in dilute NaHCO₃ solution). It should be noted, however, that these polyhydroxyl-compounds from catechol are capable of exhibiting a second colour when dissolved in excess of NaOH. This is always a very high colour, generally green, and the colour-factor is then about 1.085 for the ϵ or β hydroxyl—really the ϵ or β ionised oxygen O'. For example, di-catechol-phthalein in NaOH shows λ 652 for its absorption-band, and by theory $593 \times (0.9657)^2 \times (1.085)^2 \times 1.002 = \lambda$ 653.

It should also be noted that when guaiacol combines to a phthalein or aurine, it is probable from the evidence stated in Part IV that the —OCH₃ group is *para*- and the —OH group *meta*- to the centre instead of *vice versa*. If then the 16th colour-factor just mentioned as being equal to 1.037 and derived from these guaiacol compounds is not ϵ -methoxyl in presence of γ -hydroxyl but γ -methoxyl accompanied by β - (or ϵ -) hydroxyl, the value of that combination, previously ascertained, should agree with $1.037 \times \gamma$ -hydroxyl. Now γ -OH is 0.9657, β -OH is 1.030, and γ -OCH₃ is about 0.973. Combining these we find $1.030 \times 0.973 = 1.003$ and 1.037×0.9657

* The distinction between the positions β and ϵ is only valid when γ is not occupied by OH, and does not exist in aurine compounds.

$= 1.003$. This practically proves that in the guaiacol colours the methyl is really *para* to the central carbon-atom: it is worth noting, however, that in this formulation of guaiacol-phthalein the compound becomes a meta-quinone, a type of compound which has hitherto met with no acceptance.

The 17th colour-factor is that of the α -SO₃H group in the so-called sulphonephthaleins or sulphureins. As pointed out in Part V of this work, these substances are merely sulphonic acids of benzaurine—not phthaleins at all in the strict sense: for example, they are yellow when acid and do not combine with hydroxylamine. The value of this colour-factor is 1.018. Since the factor for the CO₂H in phenolphthalein is 1.002, the factor relating any sulphonephthalein to the corresponding phthalein is 1.016, *e.g.* λ 563 for (di)phenolsulphonephthalein when phenolphthalein is λ 554. The case of catecholsulphonephthalein may be worked out from the general formula, and is instructive. This substance contains one α -SO₃H (factor 1.018); two γ -hydroxyls (factor 0.9657); and two β - or ϵ -hydroxyls (factor 1.030). The calculated wave-length is therefore $593 \times 1.018 \times (0.9657)^2 \times (1.030)^2 = 597.3$. Observation (NaHCO₃ solution) gave λ 600. The agreement is quite good enough for such a complicated case, since there are five multipliers, each of which may be wrong by 0.0005. In the case of guaiacolsulphophthalein the observation was λ 608 and the calculation $593 \times 1.018 \times (0.973)^2 \times (1.030)^2 = 607$.

Sulphuric-acid Colours.—It should be noted that although the —SO₃H group in the molecule has a colour-factor, it is not possible to explain by means of a colour-factor the behaviour of coloured substances when dissolved in strong sulphuric acid, and it must be assumed that an oxonium-salt is formed *outside* the molecule. As shown in Parts I and VI, the sulphuric-acid colours obey the different law $\frac{1}{\lambda_1} = \frac{3}{2\lambda_0} - 0.000695$, in which λ_0 is the alkaline and λ_1 the sulphuric-acid wave-length.

I have now succeeded in extending this law, which is evidently one governing change of colour by change of ionisation at or near the colour-centre, to explain the fact that benzaurine-derivatives exhibit a third colour, *viz.* in *dilute* acid. (Thus benzaurine has λ 553 in alkali [pink], λ 473 in H₂SO₄ [orange], and λ 493 [salmon] in dilute HCl, as well as the bandless yellow colour when neutral.)

Calculation of Acid Colours of the Benzaurine Family.

	Name.	Value of λ_0 .	Calculated λ_1 .	Observed in HCl.
1	Benzaurine	553	494	493
2	Phenolsulphophthalein	563	506	507
3	Catecholsulphophthalein	600	553	557
4	Guaiacolsulphophthalein	608	564	565
5	Thymolsulphophthalein	604	558	552

Although the acid bands are abnormally broad and of somewhat uncertain centre, I do not think that this fact fully accounts for the discrepancies of the above table, but admit that there is probably some factor not taken account of which modifies the action of the frequency-law.

The abnormal colour of "crystal-violet" may next be considered: it has, of course, been the subject of active discussion for thirty-five years.

The following table exhibits the results of my observations on the "aniline dyes" in presence of alkali and acid. It should be noted in regard to the mono-derivatives of fuchsene that fuchsone is insoluble both in acid and alkali, and that fuchsimine and its dimethyl-derivative are insoluble in alkali, but soluble, with colour, in acid, with bands at about $\lambda\lambda$ 430 and 460 respectively.

A. *Di-derivatives of Fuchsene (all Para).*

Name.	Substituents.	Alkali λ .	Acid λ .	Notes.
Benzaurine	Two OH	553	494	—
Aminofuchsone	One OH, one NH_2	558	?	—
Doebner's violet	Two NH_2	—	562	Nearly neutral.
Benzaurine	Two OH	553	494	—
Dimethylaminofuchsone	One OH, one NMe_2	586	515 broad	? 500 + 530
Malachite-green	Two NMe_2	—	619	Nearly neutral.

B. *Tri-derivatives of Fuchsene (all Para).*

Name.	Substituents.	Alkali λ .	Acid λ .	Notes.
Aurine	Three OH	534	485	Also 503 + 548, then neutral.
Paeonin (aminobenzaurine)	Two OH, one NH_2	538	497	Also 518 faint.
Red corallin (Diaminofuchsone)	One OH, two NH_2	541	?	—
Pararosanine	Three NH_2	<i>nil</i> in alkali, 544 neutral	575	—
Aurine	Three OH	534	485	—
Dimethylaminobenzaurine	Two OH, one NMe_2	575	500	Interpolated.
Bis-dimethylaminofuchsone (oxymalachite-green)	One OH, two NMe_2	580	607	—
Crystal-violet	Three NMe_2	<i>nil</i> in alkali, 595 neutral	632	—

We note that the normal colour is in alkali in OH-compounds, and in acid in amino-compounds, yet nevertheless the differences in colour are regular, *e.g.* 553, 558, 561 : 553, 586, 619 : 534, 538, 541, 544 : 534, 575,

580, 607, 632. It is unfortunate that the series is incomplete; but on the existing evidence it seems that the change of colour takes one regular path in neutral solution, and another, equally regular but different, in acid solution. This amounts to the assumption that there are separate colour-factors for the ionised $-\text{NH}_3^+$ and $-\text{NHMe}_2^+$ groups different from the factors for $-\text{NH}_2$ and $-\text{NMe}_2$, and there the matter may rest until the lacunae in the evidence are filled.

There are other lacunae in a complete colour-scheme for triphenyl-carbinol-derivatives, namely, colour-factors for groups and positions which occur only once. In a special investigation of benzaurine-derivatives I have endeavoured to find approximations to the values of most of the remaining colour-factors, and the results are given below:

	Name of substance.	Source.	λ .	Name of colour-factor.	Value of factor.
1	α -bromobenzaurine .	Orthobrombenzoic acid and phenol	568	α -bromo	1.027
2	β -bromobenzaurine .	Metabrombenzoic acid and phenol	565	β -bromo	1.022
3	γ -bromobenzaurine .	Parabrombenzoic acid and phenol	539	γ -bromo	0.975
4	Phenolisophthalein .	Isophthalic acid and phenol	560	β -carboxyl	1.012
5	Phenoltterephthalein .	Terephthalic acid and phenol	550	γ -carboxyl	0.995
6	Metasulphobenzaurine	Metasulphobenzoic acid and phenol	560 (vague)	β -sulphonyl	1.01
7	Parasulphobenzaurine	Parasulphobenzoic acid and phenol	568	γ -sulphonyl	1.027*
8	ϵ -sulphobenzaurine .	Sulphonation of benzaurine	559	ϵ -sulphonyl	1.010
9	α -aminobenzaurine .	Anthranilic acid and phenol	565	α -amino	1.022
10	Michler's hydrol .	<i>cf.</i> Malachite-green	619:603	C-phenyl	1.026†

* Abnormal: less than unity expected.

† Hereby the diphenylcarbinol dyes can be calculated from fuchsene.

The δ -position in benzaurine appears to be difficult to investigate, or is possibly quite abnormal. The only substance bearing on it which I have succeeded in making is in the aurine series, and is the δ -methyl-derivative of oxymalachite green (from Michler's ketone and metacresol). This has λ 587 when basic and λ 617 when faintly acid. Malachite-green having λ 619, we see that the combination of γ -OH and α -CH₃ is almost self-extinguishing, the factor being 0.997, so that (in the aurine series) α -CH₃ ($=\delta$ -CH₃) is about 1.030, whereas from the metacresolphthaleins the value is about 1.026.

In conclusion, I wish to point out an extension of this colour-theory to dyes outside the triphenyl-carbinol series, *e. g.* the ratio of the wave-lengths of methylene-blue and thionine, $665 \div 602$, is the same as that of malachite-

green to Doebner's violet, $619 \div 561$, showing that the colour-factor for four methyl-groups applies also in the thiophenazine series of dyes.

ADDENDUM, 15/9/20.—Since the diphenylcarbinol dyes can be calculated from the triphenylcarbinol series by dividing by 1.026, we can next calculate the indamine dyes by finding a factor for the substitution of $-\text{N} =$ for $-\text{CH} =$ in the centre. This factor is about 1.20. Thus to calculate Bindschedler's green from malachite-green, first divide by 1.026, giving Michler's hydrol, then multiply by 1.20, giving tetramethylindamine: next from the indamines the oxazines and thiazines can be calculated. The factor is similar for both, about 0.90 for the oxo-linkage (also occurring in fluorescein) and 0.92 for $-\text{S}-$ linkage in methylene-blue. Methylene-blue calculated from malachite-green is $619 \div 1.026 \times 1.20 \times .92 = 665$.